Studies of Environmentally-Relevant Materials

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For 1999, our experimental work at ALS concentrated on the studies of environmentally relevant materials, including materials that can reduce toxic Tc(VII) and Cr(VI), glasses that may be used for solid nuclear waste storage, and bones of laboratory rats that were treated by intravenous injections. The experiments were carried out at the end stations of Beamlines 7.3.1.1, 8.0.1, 9.3.1, 9.3.2, and 10.3.1-2.

REDUCTION OF Tc(VII) AND Cr(VI)

Technetium (^{99}Tc) is a radioactive byproduct of nuclear fission, and its concentration in certain nuclear waste materials may set the regulatory limit for disposal. The high solubility and mobility of TcO_4^-, which can be present in both nuclear waste streams and waste forms, needs to be addressed. A solution is to reduce Tc(VII) to Tc(IV), which is much less soluble and mobile. One method is by adsorbing Tc(VII) onto surfaces of reducing agents. While previous experiments demonstrated that Tc(VII) ions were sorbed on and reduced by some materials, the products and the mechanism of sorption and reduction are not fully characterized or understood. Re has similar redox properties as Tc and can be treated as a surrogate for Tc in selected systems. Rhenium sorption samples were prepared by immersing powders of Fe metal, FeO, FeS, and FeS_2, respectively, in a 0.010 M Re(VII) solution. The reacted powders were extracted after the mixtures were centrifuged and the liquid phase decanted. Characterized Re oxide and sulfide materials were also prepared as references. The photoemission of Re 4d and 4f core levels, and NEXAFS of Re N_{III} experiments were carried out. The results reveal that the amount of absorbed Re decreases from Fe metal, through FeO, FeS, to FeS_2; and that different species of Re are sorbed on surfaces of different Fe-bearing materials, with more oxidized species tending to dominate on the less sorbed surfaces (Fig. 1).

This result is intriguing because the sulfides were thought to be more efficient than the oxide in reducing Re(VII) because the sulfide ion has higher reducing potential than the ferrous ion. The puzzle was solved after the pH values of the residual solutions were measured. The residual solutions of the sulfides have pH values of 2 to 4, while those of the Fe metal and FeO have pH values of 8 to 10. Low pH values made the sulfides less reducing and ReO_4^- sorb more easily to the surfaces, whereas high pH made the Fe and FeO more reducing and ReO_4^- does not readily sorb onto the surfaces. Thus, the photoemission and NEXAFS results, together with the pH measurements of the residual solutions, suggest that the sorption and reduction of Re on the surfaces of Fe-bearing materials are at least partially controlled by the final pH of the solution-particle mixture.

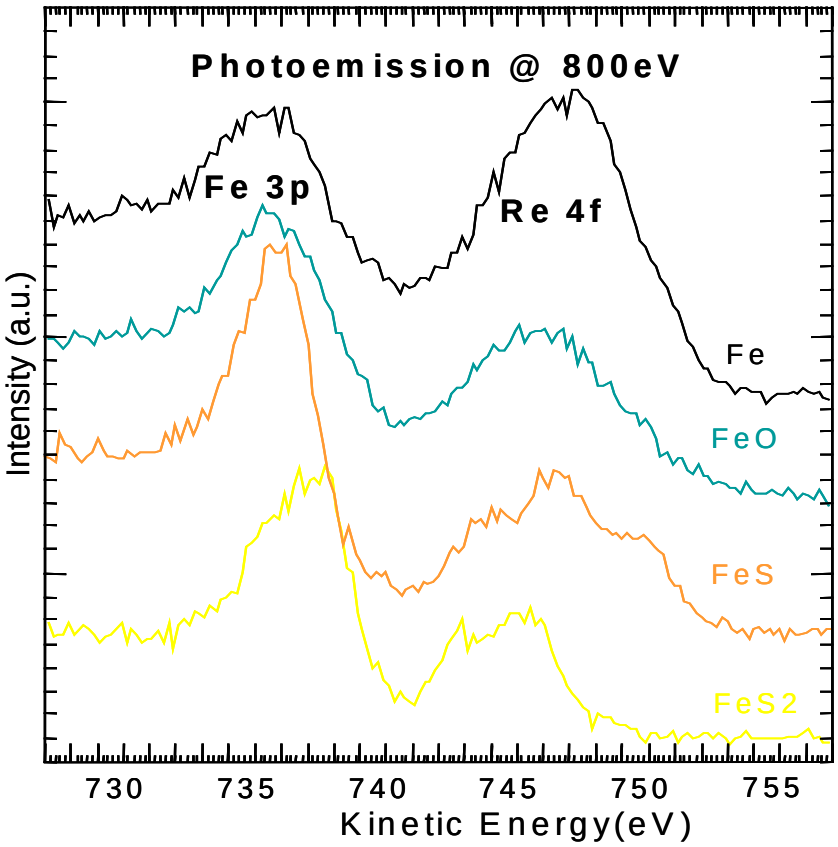

Figure 1. Re 4f photoemission spectra at the photon energy of 800 eV. The spectra were aligned relative to the C 1s feature.

Chromium (Cr) is a common contaminant in groundwater and soils due to its widespread use in a variety of industrial processes, and is highly toxic even at low concentrations. Cr(VI) is quite soluble in aqueous solution and thus mobile in groundwater and soils, while Cr(III) is much less soluble and thus less bioavailable. Previous experiments have shown that Cr(VI) could be readily reduced by magnetite to Cr(III), but there was no study on the homogeneity of the reduced Cr(III) on the magnetite surfaces. The results from our PEEM experiments show that Cr(VI) is reduced to Cr(II) on Magnetite surfaces, and the distribution of Cr on the surfaces is homogenous. The reduction result is consistent with that from previous photoemission and NEXAFS experiments, and the distribution result further elucidates the nature of the Cr surface reduction. This study illustrated that the PEEM technique is well-suited for the study of the Cr sorption onto Fe oxide surfaces.

SODIUM IN VITREOUS WASTE FORMS

We continue to determine the speciation of Na in waste from glasses using x-ray absorption fine structure techniques (near-edge and extended-XAFS) at the Na K-edge. Several formulations of waste form glasses and reference materials have been investigated using both fluorescence and electron yield techniques. Figure 2 shows the Fourier Transforms obtained from several of the Na glass waste forms. From this data, we have extracted the first shell inter-atomic Na-O distances and coordination numbers. This metrical information has been correlated to the elemental composition of the glass, NMR results, and the specific processing conditions. These results correspond accurately to the leaching behavior of the glass series we are studying.

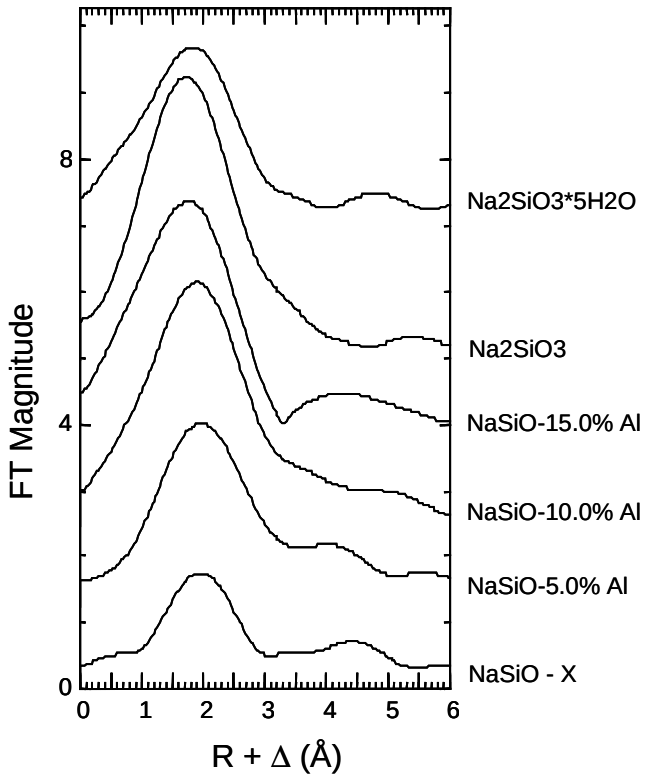

Figure 2. Fourier Transforms of the Na K-edge EXAFS obtained from a waste form glass series containing variable concentrations of sodium as denoted.

SPECIATION AND DISTRIBUTION OF Np IN MAMMALIAN BONES

We examined rat bones containing several micrograms of Np-237 that resulted from intravenous injections of Np into laboratory rats. Using the microprobe Beamline 10.3.1, we were able to obtain elemental maps from about 2μg of Np well-localized at the surface of a reference counting plate. There was not enough photon flux at the Np L_3 edge (~16.8 keV) using the beamline in the high bandpass mode to permit detection of the Np using its corresponding fluorescence line (~13 keV). The M edge fluorescence line (<4 keV) was resolved from the counting plate and an acceptable map obtained. However, due to interference from the bone matrix, we were not able to resolve the Np M edge fluorescence from that of the other bone constituents. Thus, there was no point in re-examining the Np rat bones on 10.3.2 under fully monochromatic conditions and studies of environmental materials containing Cr, Mn, and Fe were performed instead.

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